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SHORT COMMUNICATION

Biosorption of methylene blue from aqueous solutions by *Typha angustata* phytomass

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Abstract The objective of this study was to investigate the biosorption of an azo dye (Methylene blue) by a wetland phytomass (*Typha angustata*) under post-phytoremediation scenario. Thus, the phytomass was used without any chemical modification. The batch adsorption experiments were conducted to evaluate the effects of contact time and temperatures (25–45 °C) on the adsorption of methylene blue (MB) from aqueous solution by cattail phytomass (CP). More than 80 % of MB dye was removed from the aqueous solution within first 10 min of the experiment. Langmuir isotherm was modeled to describe the monolayer adsorption of MB dye ($R^2 = 0.995$) with the maximum adsorption capacity of 8.1 mg/g at 25 °C. Pseudo-second-order kinetic model adequately described the kinetics of absorption process ($R^2 = 0.999$). The adsorption of MB on the cattail phytomass was a spontaneous and endothermic process that was governed by chemisorption. Hence, CP could be applied as a potential low cost biosorbent to treat dyeing wastewater.

Keywords Biosorption · Methylene blue · Phytomass · *Typha* spp.

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Introduction

Cattail (*Typha* species) is a tall, emergent wetland weed, which is widely found in unlined water channels and water logged areas (Larkin et al. 2012). The growth of cattail is higher than other aquatic weeds, thus, poses several problems such as regime shifts, mono-dominance, litter production, and the flow disturbance in water channels (Hegazy et al. 2011; Osland et al. 2011). Moreover, it cannot be eradicated with the application of pesticides due to its pest resistance (Mahmood 2005). However, the cattails have shown their phytoremediation ability to remove various contaminants from the aquatic environment (Dordio et al. 2010; Santos-Diaz and Barron-Cruz 2011). Cattail phytomass (CP) can bioaccumulate high levels of heavy metals in its tissues without any serious physiological damage (Hegazy et al. 2011). CP turns into a potential pollution vector after phytoremediation and it requires proper disposal (Abhilash and Yunus 2011). Although studies have been conducted on various aspects of phytoremediation, yet, the disposal of contaminated phytomass has not been addressed adequately to make it a feasible technology (Dhir and Sirivastava 2012). So the used CP can either be disposed into landfills or can be subjected to anaerobic digestion for biogas production (Hu et al. 2007). Alternatively, it can be used as low-cost biosorbent by considering its highly porous structure to treat wastewater (Abdel-Ghani et al. 2009; Hu et al. 2010; Hegazy et al. 2011). Even-though untreated phytomass is constrained with lower biosorption capacity (Nasuha and Hameed 2011), yet, it is beneficial to avoid any recontamination of the environment.

Methylene blue (MB) is a cationic dye which is extensively used in dyeing industry. MB is a toxic dye

and causes several health risks in humans upon exposure such as nausea, vomiting, eye injury, and methemoglobinemia (Al-Anber et al. 2011; Dutta et al. 2011; Vucurovic et al. 2012). Thus, it is important to remove MB dye from industrial wastewater. The objective of present study was to investigate the feasibility of untreated cattail phytomass (*Typha angutata*) as a low cost biosorbent to remove MB dye from the aqueous solution. The research was conducted at Korea Advanced Institute of Science and Technology, Republic of Korea in December 2011.

Materials and methods

Preparation of adsorbent

CP used in this study was collected from a local pond in Daejeon, South Korea. The biomass was washed with tap water to remove dust and then it was washed by distilled water. The washed CP was dried at room temperature initially and was further dried in an oven at 50 °C for 24 h (Al-Anber et al. 2011). The oven dried CP was ground using lab scale grinder and sieved to obtain a particle size of less than 3 mm. The adsorbent was stored in a moisture-free environment and used without any further chemical or physical treatment in the adsorption experiments.

Preparation of dye solutions

Methylene blue was used as a model cationic dye in this experiment. MB dye (≥82 %) was purchased from a local supplier and was used without further purification. The stock solution (500 ppm) of MB dye was prepared by dissolving a 0.5 g of MB in 1 L of distilled water. The experimental solutions of desired concentration were prepared by diluting the stock solution with distilled water. The concentration of MB dye was measured at λmax = 665 nm (Sajab et al. 2011) using UV–visible spectrophotometer (Hach DR 5000).

Adsorption studies

The adsorption experiments were conducted in 250 mL flasks while volume of the dye solution was kept at 100 mL. The solution pH was kept at its original value (5.2) and was not controlled during the experiment. Adsorption equilibrium experiments were conducted by adding 0.5 g CP to 100 mL of dye solution (C_0 = 50 mg/L). The MB solutions were agitated at 150 rpm at different temperature levels (25–45 °C). Adsorption kinetic experiments were carried out at the equilibrium conditions whereas samples were withdrawn for residual dye analysis at regular intervals.

The adsorption capacity (q_e) and color removal efficiency (R) were calculated using following Eqs. (1) and (2), respectively.

$$q_e(\text{mg/g}) = (C_o - C_t)\, V/M \quad (1)$$

$$R(\%) = (C_0 - C_t)100/C_0 \quad (2)$$

where C_0 is the initial dye concentration (mg/L) and C_t is the residual concentration of the dye (mg/L) at different time intervals, V is the volume of the aqueous solution (L), and M is the mass of the biosorbent (g).

Results and discussion

Effect of contact time and temperature

The effect of contact time and temperature on the adsorption of MB by CP is presented in Fig. 1. It was apparent that dye removal was a function of contact time and temperature. The adsorption of MB onto CP approached equilibrium after around 120 min. The amount of MB dye adsorbed at equilibrium was found in a range of 7.8–7.9 mg/g at all the tested temperature levels. It was also evident that almost 80 % of MB dye was removed during the first 10 min of the process at all temperature levels and only 10 % improvement was observed till the equilibrium was reached. ANOVA test revealed that the both contact time ($p < 0.001$) and temperature ($p < 0.012$) showed a significant effect on the dye removal. Similar results were reported in literature (Nasuha et al. 2010; Hu et al. 2010; Safa and Bhatti 2011), where the dye removal was found as a function of contact time and temperature. Higher rate of dye removal was observed during the initial phase of adsorption due to the availability

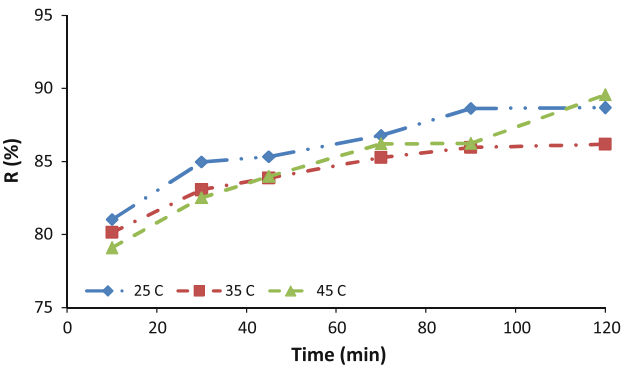

Fig. 1 Effect of contact time and temperature on the removal of MB dye by cattail phytomass

of free sites on the upper surface of the biosorbent. First phase of higher removal rate was followed by a phase of slow dye removal and only little improvement was observed close to the equilibrium stage (Safa and Bhatti 2011). The slow adsorption phase could be due to the filling of free binding sites during first stage that caused a possible repulsion among the adsorbed molecules and molecules present in aqueous solution (Akar et al. 2009; Vucurovic et al. 2012).

Adsorption kinetics

The dynamics and mechanism of adsorption can be understood by evaluating the kinetic data. Three stages may be involved during the adsorption of dye molecules such as migration of MB molecules to the outer surface of the CP particles, molecular and pore diffusion. More than one stage may be involved in the adsorption of dye molecules (Safa and Bhatti 2011).

Three kinetic models; pseudo-first order, pseudo-second order, and intra-particle diffusion are widely applied to evaluate the kinetics of the adsorption process (Hu et al. 2010). However, it was found that pseudo-first-order model did not fit well to this study (data not shown) complying with literature (Hu et al. 2010; Vucurovic et al. 2012). Thus, kinetic data were subjected to pseudo-second order and intra-particle diffusion equations as shown in Fig. 2. These models are given in Eqs. (3) and (4).

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (3)$$

$$q_t = K_{pi} t^{1/2} + C_i \quad (4)$$

where q_t (mg/g) is the adsorption capacity at any time t, k_2 (g/mg.min) is the second order rate constant, K_{pi} (mg/g.min$^{1/2}$) is the intra-particle diffusion rate constant and C_i is the boundary layer thickness. Pseudo-second-order model was applied by plotting t/q_t versus t and model parameters; rate constant (k_2) and initial adsorption rate ($h = k_2 q_e^2$) were calculated from the intercept of the plot. These parameters are given in Table 1. The values of R^2 for all the temperature levels were higher than 0.999 and adequately fitted to the pseudo-second-order model. Figure 2a clearly displayed that the pseudo-second-order model was quite linear over the entire range of the experimental values. The fitness of this model was further verified by calculating normalized standard deviation (Δq) that was given in Eq. (5).

$$\Delta q\,(\%) = \sqrt{\sum \frac{\left[(q_{t,\mathrm{exp}} - q_{t,\mathrm{cal}})/q_{t,\mathrm{exp}}\right]^2}{n-1}} \times 100 \quad (5)$$

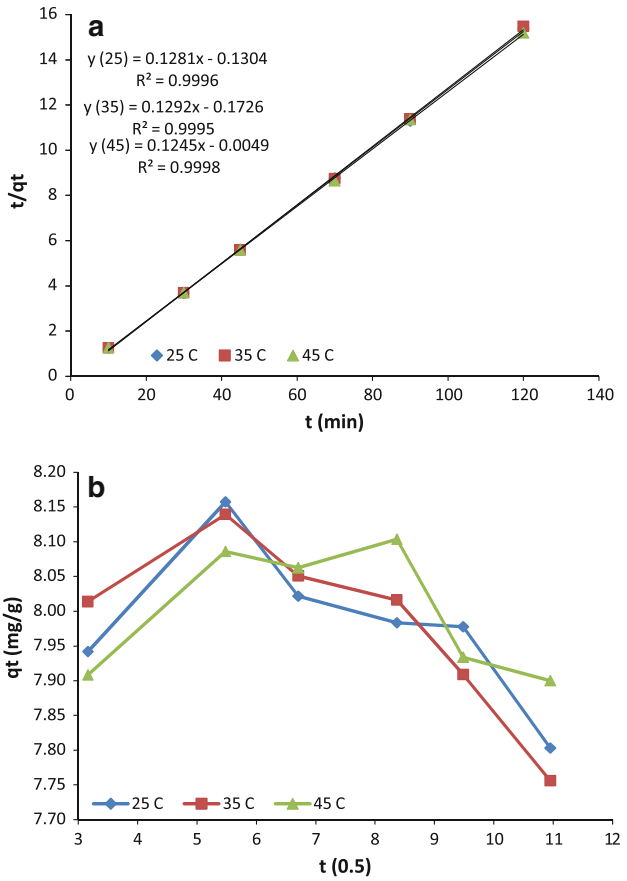

Fig. 2 Adsorption kinetics of MB dye on cattail biomass at various temperatures. **a** Pseudo-second-order model, **b** intra-particle diffusion model

where $q_{t,\mathrm{exp}}$ and $q_{t,\mathrm{cal}}$ represent experimental and calculated values of q and n is the total number of data points. Higher value of R^2 and lower value of Δq show the fitness of kinetic model. R^2 values (>0.999) and Δq values (<2 %) verified the validity of pseudo-second-order model to explain the adsorption of MB dye on CP (Zhang et al. 2011). Thus, the dynamics of adsorption process was adequately described by the pseudo-second-order model, and chemisorption was found the rate-controlling step as reported in literature (Dutta et al. 2011; Deng et al. 2011; Vucurovic et al. 2012).

Pore and intra-particle diffusion model was also applied to investigate any possible role of diffusion in the mechanism of MB adsorption on CP (Hu et al. 2010; Vucurovic et al. 2012) as shown in Fig. 2b. It was observed that the response was linear initially to some extent, but linearity could not be sustained later on. The overall response could be divided into three stages. However, the plot lines did not pass through the origin, for any temperature implying that the intra-particle

Table 1 Kinetic parameters of pseudo-second order and intra-particle diffusion models

Temperature	q_{exp}	q_e	k_2	h	R^2	C_i	Δq (%)
25	7.98	7.806	0.1258	7.669	0.9996	8.135	1.44
35	7.91	7.740	0.0967	5.794	0.9995	8.24	1.91
45	7.93	8.032	3.1633	204.082	0.9998	8.03	1.2

diffusion was not the rate-limiting step in MB adsorption process (Safa and Bhatti 2011). Hence, the adsorption of MB dye was mainly governed by chemisorption along with inter-particle diffusion (Akar et al. 2009; Safa and Bhatti 2011; Vucurovic et al. 2012).

Equilibrium studies

Adsorption isotherm studies are conducted to find out relationship between the amount of dye adsorbed per unit mass of the biosorbent and the residual concentration of dye present in the solution. Several models are applied for this kind of investigations. The most common types are Langmuir and Freundlich isotherm models (Nasuha and Hameed 2011) which are given by Eqs. (6) and (7), respectively.

$$C_e/q_e = C_e/q_m + 1/K_a q_m \quad (6)$$

$$\ln q_e = \ln K_F + \ln C_e/n \quad (7)$$

where q_m is the maximum adsorption capacity in monolayer adsorption, K_a is the adsorption equilibrium constant (L/mg) related to free energy of adsorption, K_F is Freundlich isotherm constant (mg/g) related to bonding energy and the value of n describes the adsorption intensity. The parameters of the both models are presented in Table 2.

Higher value of $R^2 > 0.995$ for Langmuir isotherm model was noticed. The validity of Langmuir model to adsorption data verified the finding of kinetic evaluation; the adsorption of MB dye on CP was mainly governed by chemisorption mechanism (Safa and Bhatti 2011). Besides mechanistic description, this model also provided the information about the feasibility of adsorption process through a dimensionless constant; separation factor (R_L) given in Eq. (8).

$$R_L = 1/(1 + K_a C_0) \quad (8)$$

Safa and Bhatti (2011) reported that the adsorption process would be considered favorable if R_L follows $0 < R_L < 1$. In this study, the values of R_L obtained were in the range of 0–1 which implied that the adsorption of MB dye was favorable by CP (Hu et al. 2010). Freundlich isotherm model was not fitted accurately to the adsorption data ($R^2 = 0.85$) as compared to Langmuir model. The values of both the model parameters are given in Table 2.

Thermodynamic studies

The effect of temperature on the adsorption process of MB dye can further be explained by thermodynamic investigation. Thermodynamic parameters such as standard Gibbs free energy ($\Delta\mathring{G}$), standard enthalpy change ($\Delta\mathring{H}$) and standard entropy change ($\Delta\mathring{S}$) are calculated using the following equations (Nasuha and Hameed 2011).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

$$\ln K_D = -\Delta H^0/RT + \Delta S^0/R \quad (10)$$

where R is the ideal gas constant (8.314 J/mol.K), T is the absolute temperature in kelvin, $K_D = Cs/Ce$ is the distribution coefficient and C_s is the equilibrium concentration (mg/L) of MB dye adsorbed on CP (Hu et al. 2010). Thermodynamic parameters were calculated from

Table 2 Adsorption isotherm constant for MB dye on cattail biomass

Model	Parameters	Temperature	
		25 °C	45 °C
Langmuir	q_m (mg/g)	8.10	7.96
	K_a (L/mg)	9.64	27.91
	R_L	0.002	0.0007
	R^2	0.9955	0.9974
Freundlich	K_F	6.927	7.287
	n	12.42	21.09
	R^2	0.832	0.863

the plot of $\ln K_D$ versus $1/T$. The increase in temperature resulted in the decreased value of distribution coefficient. The overall ΔG° values were found negative (−842, −970, −1098 J/mol) for three temperature levels. These negative values concluded that the adsorption process was spontaneous (Al-Anber et al. 2011). However, positive value of ΔH° (2984 J/mol) indicated the endothermic nature of the adsorption process (Nasuha and Hameed 2011; Safa and Bhatti 2011). The positive value of ΔS° (12.84 J/mol.k) showed an increase in the randomness at the dye-CP interface. This randomness could affect the adsorption process either by desorbing dye or removing water molecules from the CP surface (Malkoc and Nuhoglu 2007).

Conclusion

This study investigated the feasibility for the removal of MB dye by a wetland phytomass (*Typha angustata)* from the aqueous solution with an aim to use this biomass after phytoremediation. The removal efficiency of MB dye increased with increasing contact time (0–120 min) and temperature (25–45 °C). The equilibrium was approached after around 120 min. The adsorption kinetic evaluation was well described by pseudo-second-order model ($R^2 > 0.999$) for the adsorption of MB dye on CP. Intra-particle diffusion model showed that several types of mass transfer mechanisms were involved; however, chemisorption was the major rate-limiting step. Equilibrium studies showed that the adsorption process was explained by the Langmuir model ($R^2 > 0.995$). The maximum adsorption capacity of MB dye on CP was about 8.01 mg/g at 25 °C. Both the kinetic and equilibrium studies suggested that the removal of MB dye from aqueous solution by cattail biomass was mainly governed by chemisorption. Thermodynamic evaluation showed that the removal of MB dye was spontaneous and endothermic process. These results suggest that CP is a potential low-cost adsorbent for the dye removal from industrial wastewater.

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References

Abdel-Ghani NT, Hegazy AK, El-Chaghaby GA, Lima EC (2009) Factorial experimental design for biosorption of iron and zinc using *Typha domingensis* phytomass. Desalination 249:343–347

Abhilash PC, Yunus M (2011) Can we use biomass produced from phytoremediation? Biomass Bioenerg 35:1371–1372

Akar T, Anilan B, Gorgulu A, Akar ST (2009) Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: *Pyracantha coccinea* berries. J Hazard Mater 168:1302–1309

Al-Anber ZA, Al-Anber MA, Matouq M, Al-Ayed O, Omari NM (2011) Defatted Jojoba for the removal of methylene blue from aqueous solution: Thermodynamic and kinetic studies. Desalination 276:169–174

Deng H, Lu J, Li G, Zhang G, Wang X (2011) Adsorption of methylene blue on adsorbent materials produced from cotton stalk. Chem Eng J 172:326–334

Dhir B, Sirivastava S (2012) Disposal of metal treated salvinia biomass in soil and its effect on growth and photosynthetic efficiency of wheat. Int J Phytoremediat 14:24–34

Dordio A, Carvalho AJP, Teixeira DMT, Dias CBD, Pinto AP (2010) Removal of pharmaceuticals in microcosm constructed wetlands using *Typha* spp. and LECA. Bioresour Technol 101:886–892

Dutta S, Bhattacharyya A, Ganguly A, Gupta S, Basu S (2011) Application of Response Surface Methodology for preparation of low-cost adsorbent from citrus fruit peel and for removal of Methylene Blue. Desalination 275:26–36

Hegazy AK, Abdel-Ghani NT, El-Chaghaby GA (2011) Phytoremediation of industrial wastewater potentiality by *Typha domingensis*. Int J Environ Sci Tech 8:639–648

Hu ZH, Yu HQ, Yue ZB, Harada H, Li YY et al (2007) Kinetic analysis of anaerobic digestion of cattail by rumen microbes in a modified UASB reactor. Biochem Eng J 37:219–225

Hu Z, Chen H, Ji F, Yuan S (2010) Removal of Congo Red from aqueous solution by cattail root. J Hazard Mater 173:292–297

Larkin DJ, Lishawa SC, Tuchman NC (2012) Appropriation of nitrogen by the invasive cattail Typha × glauca. Aquat Bot. doi: 10.1016/j.aquabot.2012.03.001

Mahmood TZ (2005) Integrated management of cattails in water carriage ways of Pakistan. Pak J Weed Sci Res 11:85–89

Malkoc E, Nuhoglu Y (2007) Determination of kinetic and equilibrium parameters of the batch adsorption Cr (IV) onto waste acorn of Quercus ithaburensis. Chem Eng Process 46:1020–1029

Nasuha N, Hameed BH (2011) Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea. Chem Eng J 166:783–786

Nasuha N, Hameed BH, Din ATM (2010) Rejected tea as a potential low-cost adsorbent for the removal of methylene blue. J Hazard Mater 175:126–132

Osland MJ, Gonzalez E, Richardson CJ (2011) Restoring diversity after cattail expansion: disturbance, resilience, and seasonality in a tropical dry wetland. Ecol Appl 21:715–728

Safa Y, Bhatti HN (2011) Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. Desalination 272:313–322

Sajab MS, Chia CH, Zakaria S, Jani SM, Ayob MK, Chee KL, Khiew PS, Chiu WS (2011) Citric acid modified kenaf core fibres for removal of methylene blue from aqueous solution. Bioresour Technol 102:7237–7243

Santos-Diaz MDS, Barron-Cruz MDC (2011) Lead, chromium and manganese removal by in vitro root cultures of two aquatic macrophytes species: *Typha latifolia l.* and *Scirpus americanus pers*. Int J Phytoremediat 13:538–551

Vucurovic VM, Razmovski RN, Tekic MN (2012) Methylene blue (cationic dye) adsorption onto sugar beet pulp: equilibrium isotherm and kinetic studies. J Taiwan Inst Chem E 43:108–111

Zhang W, Yan H, Li H, Jiang Z, Dong L, Kan X, Yang H, Li A, Cheng R (2011) Removal of dyes from aqueous solutions by straw based adsorbents: batch and column studies. Chem Eng J 168:1120–1127